UPLAZ

A PROGRAM TO CALCULATE THE COMPOSITION OF AN URANIUM PLASMA

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ABSTRACT

UPLAZ calculates the composition of an uranium plasma as a function of plasma temperature and pressure. The plasma is assumed to be in local thermodynamic equilibrium. Iso-electronic ground state statistical weights are used as uranium ion electronic partition functions. Corrections for the lowering of atomic and ionic ionization potentials are included. A maximum of twelve degrees of ionization can be calculated. This limits the program to maximum temperatures in the range of 90,000 °K to 150,000 °K, depending on the pressure. The individual plasma species are computed in terms of particle density, partial pressure, and percent of total particles.

The program is written in FORTRAN IV for the IBM 360/50.

PHYSICAL PROBLEM

In performing a nuclear analysis or radiative heat transfer analysis of the high temperature gaseous-core or cavity reactor types, the plasma effects in the gaseous core region become important at temperatures above a few thousand degrees Kelvin. In order to account for these effects, it is necessary to determine the composition of an uranium plasma as a function of plasma temperature and pressure.

MATHEMATICAL FORMULATION

Basic Equations for Arbitrary Temperatures

An uranium plasma in local thermodynamic equilibrium is characterized by the following set of equilibrium ionization and recombination reactions. A maximum of twelve degrees of ionization is considered.

$$
\begin{array}{c}
U^{o} \rightleftarrows U^{+} + e \\
U^{+} \rightleftarrows U^{++} + e \\
U^{++} \rightleftarrows U^{+++} + e \\
\Big| \\
U^{i+} \rightleftarrows U^{(i+1)+} + e \\
\Big| \\
U^{11+} \rightleftarrows U^{12+} + e
\end{array}
\qquad (1)
$$

where

U^{o} = neutral uranium atom

U^{i} = i - times ionized uranium ion

e = electron

The relation between the number of ions and electrons in an equilibrium ionization-recombination reaction is described by the following Saha equation.

$$\frac{N_{i+1} N_e}{N_i} = 2 \left(\frac{2\pi m_e k T}{h^2}\right)^{3/2} \frac{u_{i+1}}{u_i} e^{-E_i/kT} \qquad (2)$$

where

N_{i+1} = density of (i+1) - times ionized uranium

N_i = density of i - times ionized uranium

N_e = density of electrons

m_e = electron mass

k = Boltzmann's constant

h = Planck's constant

T = plasma temperature

u_{i+1} = partition function of (i+1) - times ionized uranium

u_i = partition function of i - times ionized uranium

E_i = ionization potential for the reaction

$$U^{i+} \rightarrow U^{(i+1)+} + e$$

Due to the electrical neutrality of the plasma, the net charge is zero. This balance is expressed as

Total negative charge of electrons = Total positive charge of ions

$$N_e = \sum_{i=0}^{12} Z_i N_i \qquad (3)$$

where

Z_i = charge of i-th uranium ion.

The temperature, pressure, and total particle density are related by the equation of state for a perfect gas. The total pressure is the sum of the partial pressures of the individual species as given by

$$P = \sum_i P_i$$

$$N_{TOT}\, kT = \sum_i N_i kT = N_e kT + \sum_{i=0}^{12} N_i kT$$
$$N_{TOT} = N_e + \sum_{i=0}^{12} N_i \qquad (4)$$

where N_{TOT} = total particle density.

The right side of the Saha equation (2) is dependent on the temperature and is given by

$$K_i(T) \equiv 2 \left(\frac{2\pi\, m_e\, k\, T}{h^2}\right)^{3/2} \frac{u_{i+1}}{u_i}\, e^{-E_i/kT} \qquad (5)$$

The i-th Saha equation is then written as

$$\frac{N_{i+1}\, N_e}{N_i} = K_i(T) \qquad (6)$$

Combining (3), (4), and (6) gives the complete set of equations describing the plasma composition.

$$\frac{N_2 N_e}{N_1} = K_1 \qquad (7\text{-}1)$$

$$\frac{N_3 N_e}{N_2} = K_2 \qquad (7\text{-}2)$$

$$\frac{N_{i+1}N_e}{N_i} = K_i \qquad (7\text{-}i)$$

$$\frac{N_{13}N_e}{N_{12}} = K_{12} \qquad (7\text{-}12)$$

$$N_e = \sum_{i=1}^{13} Z_i N_i \qquad (7\text{-}13)$$

$$N_{TOT} = N_e + \sum_{i=1}^{13} N_i \qquad (7\text{-}14)$$

Note that each uranium index (i) has been increased by one, so that within the formulation of the numerical expressions of the program, the following definitions are used.

N_1 = density of U^o in particles/cc

N_2 = density of U^+ in particles/cc

N_{13} = density of U^{12+} in particles/cc.

Since the electrons and various uranium species will have numerical values in the approximate range of 0 - 10^{20} particles/cc, the set of equations (7-1) through (7-14) is scaled so that all particle density can be expressed as dimensionless variables, C_i, where $0 \leq C_i \leq 1$. Dividing each term in (7-1) through (7-14) by N_{TOT} gives the following set of scaled equations.

$$\frac{C_2 C_e}{C_1} = K_1^* \tag{8-1}$$

$$\frac{C_3 C_e}{C_2} = K_2^* \tag{8-2}$$

$$\vdots$$

$$\frac{C_{i+1} C_e}{C_i} = K_i^* \tag{8-i}$$

$$\vdots$$

$$\frac{C_{13} C_e}{C_{12}} = K_{12}^* \tag{8-12}$$

$$C_e = \sum_{i=1}^{13} z_i C_i \tag{8-13}$$

$$1 = C_e + \sum_{i=1}^{13} C_i \tag{8-14}$$

where

$$C_i = \frac{N_i}{N_{TOT}}$$

$$C_e = \frac{N_e}{N_{TOT}}$$

$$K_i^* = \frac{K_i}{N_{TOT}} \tag{9}$$

From (8-1) through (8-12),

$$C_2 = \frac{C_1}{C_e} K_1^*$$

$$C_3 = \frac{C_2}{C_e} K_2^* = \frac{C_1}{C_e^2} K_1^* K_2^* = \frac{C_1}{C_e^2} K_2'$$

$$C_4 = \frac{C_3}{C_e} K_3^* = \frac{C_1}{C_e^3} K_1^* K_2^* K_3^* = \frac{C_1}{C_e^3} K_3'$$

In general,

$$C_i = \frac{C_{i-1}}{C_e} K_{i-1}^* = \frac{C_1}{C_e^{\,i-1}} K_1^* K_2^* \ldots K_{i-1}^* = \frac{C_1}{C_e^{\,i-1}} K'_{i-1} \tag{10}$$

where

$$K'_i = \prod_{j=1}^{i} K_j^* \quad . \tag{11}$$

From (8-13) and (9),

$$C_e = \sum_{i=1}^{13} Z_i C_i = \sum_{i=2}^{13} Z_i \frac{C_1}{C_e^{\,i-1}} K'_{i-1} = C_1 \sum_{i=2}^{13} \frac{Z_i}{C_e^{\,i-1}} K'_{i-1} \tag{12}$$

From (8-14) and (9)

$$1 = C_e + \sum_{i=1}^{13} C_i = C_e + C_1 + \sum_{i=2}^{13} C_i$$

$$1 = C_e + C_1 \left(1 + \sum_{i=2}^{13} \frac{K'_{i-1}}{C_e^{\,i-1}}\right) \tag{13}$$

Solving for C_1 from (10) and (11) and equating the results,

$$C_1 = \frac{C_e}{\sum_{i=2}^{13} Z_i \frac{K'_{i-1}}{C_e^{\,i-1}}} = \frac{1-C_e}{1 + \sum_{i=2}^{13} \frac{K'_{i-1}}{C_e^{\,i-1}}} \tag{14}$$

or

$$F(P,T,C_e) = \frac{C_e}{\sum_{i=2}^{13} Z_i \frac{K'_{i-1}}{C_e^{\,i-1}}} + \frac{C_e - 1}{1 + \sum_{i=2}^{13} \frac{K'_{i-1}}{C_e^{\,i-1}}} \tag{15}$$

For a given temperature and pressure, $F(P,T,C_e) = F(C_e)$ becomes a polynomial function in C_e. Equation (16) is solved by an iteractive method. The solution gives the electron fraction C_e.

$$\frac{C_e}{\sum_{i=2}^{13} Z_i \frac{K'_{i-1}}{C_e^{\,i-1}}} + \frac{C_e - 1}{1 + \sum_{i=2}^{13} \frac{K'_{i-1}}{C_e^{\,i-1}}} = 0 \tag{16}$$

The electron density is given by $N_e = C_e N_{TOT}$.

From (12), $C_1 = \dfrac{C_1}{\sum_{i=2}^{13} Z_i \frac{K'_{i-1}}{C_e^{\,i-1}}}$ and $N_1 = C_1 N_{TOT}$.

From (7-i), $N_{i+1} = \dfrac{K_i}{N_i} N_e$ for $i = 1, 2, \ldots\ldots, 13$, gives the particles densities $N_2, N_3, \ldots\ldots, N_{13}$. The particle densities $N_e, N_1, N_2, \ldots\ldots, N_{13}$, then completely describe the uranium plasma composition.

Low Temperature Equations

For temperatures less than 10,000°K, the iterative method for solving equation (14) does not readily converge. Although uranium is not highly ionized at temperatures below 10,000°K, a knowledge of the low temperature uranium plasma composition is necessary in order to describe initial or startup conditions in a gaseous-core reactor. A different mathematical formulation is used to calculate the plasma composition at low temperatures.

In the temperature range from 1000°K to 10,000°K, the only species that are present in significant quantities are U^o, U^+, and e. A single reaction accounts for the equilibrium ionization and recombination of these three species

$$U^o \rightleftarrows U^+ + e \tag{17}$$

The corresponding Saha equation is

$$\frac{U^+ \, e}{U^o} = 2 \left(\frac{2\pi \, m_e \, k \, T}{h^2}\right)^{3/2} \frac{u(U^+)}{u(U^o)} \, e^{-E_o/kT} \tag{18}$$

The total particle density is

$$N_{TOT} = \frac{P}{kT} = U^o + U^+ + e \tag{19}$$

The charge neutrality is given by

$$U^+ = e \tag{20}$$

Using $N_1 = U^{o}$, $N_2 = U^{+}$, $N_e = e$, and

$$K = 2 \left(\frac{2\pi\, m_e\, k\, T}{h^2}\right)^{3/2} \frac{u(U^{+})}{u(U^{o})}\, e^{-E_o/kT} ,$$

(18), (19) and (20) are simplified as

$$\frac{N_2 N_e}{N_1} = K \tag{21}$$

$$N_{TOT} = N_1 + N_2 + N_e \tag{22}$$

$$N_2 = N_e \tag{23}$$

Dividing each term in (21), (22) and (23) by N_{TOT} and combining these equations gives

$$C_e^{\,2} + 2K^{*} C_e - K^{*} = 0 \tag{24}$$

where

$$K^{*} = \frac{K}{N_{TOT}} .$$

The solutions of (22) are

$$C_e = K^{*} \left(-1 \pm \sqrt{1 + \frac{1}{K^{*}}}\right) .$$

Since $K^{*} > 0$, $\sqrt{1 + \frac{1}{K^{*}}} > 1$ and the positive radical must be used to give a positive value of the electron concentration. The low temperature plasma composition is then given by

$$N_e = N_{TOT}\, K^{*} \left(- 1 + \quad 1 + \frac{1}{K^{*}}\right) \tag{25}$$

$$N_1 = N_{TOT} - 2N_e \tag{26}$$

$$N_2 = N_e \tag{27}$$

Uranium Partition Functions

The partition functions appearing in the general Saha equation (2) are functions of the plasma temperature and the electron configuration of the uranium atom or ion. The electronic partition function of i - times ionized uranium is given by

$$\begin{aligned} U_i &= \sum_{j=0}^{\infty} g_{i,j}\, e^{-\chi_{i,j}/kT} \\ &= g_{i,o} + g_{i,1}\, e^{-\chi_{i,1}/kT} + g_{i,2}\, e^{-\chi_{i,2}/kT} + \ldots\ldots \end{aligned} \tag{28}$$

where

$g_{i',j}$ = statistical weight of the j-th term of i - times ionized uranium

$\chi_{i,j}$ = exitation energy level of the j-th term of i - times ionized uranium

The ground state statistical weight for the i - times ionized uranium is [6]

$$g_{i,o} = (2L_{i,o} + 1)(2S_{i,o} + 1) \tag{29}$$

where

$S_{i,o}$ = spin angular momentum of ground state ion

$L_{i,o}$ = orbital angular momentum of ground state ion.

Since experimental data from which $L_{i,o}$ and $S_{i,o}$ could be determined are not presently available, the iso-electronic approximation is used to calculate the ground state statistical weights.[7] For a particular uranium ion, the $L_{i,o}$ and $S_{i,o}$ values of the neutral item which has the same number of orbital electrons as the uranium ion, are used to calculate $g_{i,o}$.

When (a) the higher energy levels are widely separated, or (b) the plasma temperature is low, or (c) the statistical weights of higher levels are small, then the higher terms in the series (26) are negligible. Under any of these conditions the ground state statistical weight is a good approximation to the partition function. For a uranium plasma, it is desirable to operate at high temperatures. From rather extensive spectroscopic data [3], it is seen that the first energy level of U^o is less than 0.01 ev above the ground state and also that the statistical weights do not become negligible. Thus it appears that conditions (a), (b) and (c) are not satisfied and thus the partition function should contain higher terms. Many of these terms can be evaluated from the data of Ref. 3. However, since the energy levels and statistical weights of the excited states are currently available only for U^o, this program uses the ground state statistical weight as the partition function for the uranium atom and all uranium ions. If higher terms were used for the U^o partition function while only the ground state terms were used for the ions, the error would be greater than the error incurred by the present approximation.

Lowering of Ionization Potentials

The uncorrected ionization potentials, as given in the Appendix, represent the energy required for the ionization of an isolated uranium atom or ion. At high pressures the plasma density increases until the atoms and ions can no longer be considered as isolated. The ionization reaction is then influenced by plasma microfields associated with electrostatic polarization (Debye effect) and interactions between neighboring charged species (lattice effect). The total effect is a lowering of the energy required for ionization of each species, the effect increasing with increasing ion charge. Corrections are made for this potential lowering by using an effective ionization potential, E^{eff},

which is computed as

$$E_i^{eff} = E_i - \Delta E_i \tag{30}$$

for the reaction $U^{i+} \rightarrow U^{(i+1)+} + e$

where

E_i = uncorrected ionization potential

ΔE_i = lowering of ionization potential.

The amount of lowering is given by

$$\Delta E_i = 2(Z_i + 1)\ e^3\ (\pi/kT)^{1/2}\ (N_e + \sum_{i=2}^{13} Z_i{}^2 N_i)^{1/2} \tag{31}$$

where

Z_i = charge of i-th ion

e = electrostatic charge of the electron

N_e = electron density

N_i = i-th ion density.

PROGRAM DESCRIPTION

The calculation flow of UPLAZ is as follows:

1. Input data is read in and printed out.
2. Total particle density and the exponential factors $T_i = \exp(-E_i/kT)$ are calculated.
3. Partition functions are determined and the functions $K_i(T)$ are calculated using (5).
4. The functions $K_i^*(T)$ and $K_i'(T)$ are evaluated using (9) and (11).
5. Equation (16) is solved by iterating on the electron fraction, C_e.
6. The particle density of each species is calculated.
7. The lowering of the ionization potential of each species is determined from (31).
8. Steps 2 through 8 are repeated using the corrected ionization potentials.

INPUT AND OUTPUT DATA

The input data consists of one card containing the pressure and temperature in 2E12.6 format as follows:

<u>Columns 1-12</u> P(atmospheres)

<u>Columns 13-24</u> T(°K).

Multiple cases can be run by consecutively stacking one data card per case.

The output data includes the total particle density, maximum degree of ionization, lowering of ionization potentials in ev, and the number density, partial pressure, and per cent of U^o, U^+, U^{++}, ..., U^{12+} and e.

SAMPLE PROBLEM

The uranium plasma composition was calculated for a pressure of 100 atmospheres and a temperature of 50,000°K. The resulting printout is given on pages 20 and 21. The calculated total pressure, total per cent, and per cent difference in positive and negative charge indicate the computational degree of accuracy.

COMPOSITION OF URANIUM PLASMA

PRESSURE (ATMOSPHERES)	TEMPERATURE (DEGREES KELVIN)
0.100000E03	0.500000E05

TOTAL PARTICLE DENSITY = 0.14676E20/cc

12 LEVELS OF IONIZATION CAN BE CALCULATED

	CONV CE	SL	SR
.1	0.768991E00	0.176856E08	0.159557E08
.01	0.784584E00	0.152669E08	0.151188E08
.005	0.785360E00	0.151543E08	0.150789E08

LOWERING OF IONIZATION POTENTIAL

ION	DELTA E(I)
1	0.69675E00
2	0.13934E01
3	0.20903E01
4	0.27870E01
5	0.34838E01
6	0.41805E01
7	0.48773E01
8	0.55740E01
9	0.62708E01
10	0.69675E01
11	0.76643E01
12	0.83610E01
13	0.90578E01

12 LEVELS OF IONIZATION CAN BE CALCULATED

	CONV CE	SL	SR
.1	0.789360E00	0.814369E08	0.736952E08
.01	0.803554E00	0.703522E08	0.696904E08
.005	0.804241E00	0.698499E08	0.695044E08

PLASMA COMPOSITION IN PARTICLES/CC

LOWERING OF IONIZATION POTENTIAL INCLUDED

	U0	U1+	U2+	U3+	U4+	U5+	U6+
	.33080E11	.31483E14	.80245E16	.75271E18	.97266E18	.11139E19	.11469E17
PER CENT	.2254E-6	.2145E-3	.5468E-1	.5129E+1	.6627E+1	.7590E+1	.7815E-1
PAR PRES	.2254E-6	.2145E-3	.5468E-1	.5129E+1	.6627E+1	.7590E+1	.7815E-1

	U7+	U8+	U9+	U10+	U11+	U12+	E
	.46443E13	.31058E8	.34316E1	.10703E-6	0.0	0.0	.11803E20
PER CENT	.3164E-4	.2116E-9	.2338E-16	.7293E-24	0.0	0.0	.8042E2
PAR PRES	.3164E-4	.2116E-9	.2338E-16	.7293E-24	0.0	0.0	.8042E2

TOTAL PRESSURE = 0.99903E2 ATMOSPHERES

TOTAL PER CENT = 0.99903E2

POSITIVE CHARGE = 0.11803E20

NEGATIVE CHARGW = 0.11803E20 PER CENT DIFF. = 0.37261E-4

APPENDIX

The theoretical ionization potentials used by the program are values which were calculated by J. T. Waber, D. Liberman, and D. T. Cromer [1]. These values are as follows:

Atom or Ion	Ionization Potential (ev)
U	6.11
U^{+}	11.46
U^{++}	17.94
U^{3+}	31.14
U^{4+}	46.03
U^{5+}	61.82
U^{6+}	87.93
U^{7+}	101.1
U^{8+}	115.0
U^{9+}	128.9
U^{10+}	157.9
U^{11+}	178.5

The ionization potentials are successive rather than cumulative, i.e., the ionization potential for U^{9+} is the energy for the reaction

$$U^{9+} \rightarrow U^{10+} + e$$

The iso-electronic ground state statistical weights used by the program are as follows: [2]

Atom or Ion	Ground State Statistical Weight ($g_{i,o}$)
U	85
U^{+}	52
U^{++}	21
U^{3+}	10
U^{4+}	1
U^{5+}	2
U^{6+}	1
U^{7+}	6
U^{8+}	9
U^{9+}	4
U^{10+}	9
U^{11+}	6
U^{12+}	1

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